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Implications of speciation on rare earth element toxicity: a focus on organic matter influence in *Daphnia magna* standard test

Nicolas Lachaux\textsuperscript{a,b,*}, Charlotte Catrouillet\textsuperscript{c}, Rémi Marsac\textsuperscript{c}, Laurence Poirier\textsuperscript{d}, Sandrine Pain-Devin\textsuperscript{a,b}, Elisabeth Maria Gross\textsuperscript{a,b}, Laure Giamberini\textsuperscript{a,b}

\textsuperscript{a}Université de Lorraine, CNRS, LIEC, F-57000 Metz, France
\textsuperscript{b}LTSER-Zone Atelier Moselle, F-57000 Metz, France
\textsuperscript{c}Géosciences Rennes, University Rennes, CNRS, UMR 6118, 35000 Rennes, France
\textsuperscript{d}Nantes University, Institut des Substances et Organismes de la Mer, ISOMer, UR 2160, F-44000 Nantes, France

E-mail contact: nicolas.lachaux@univ-lorraine.fr

Abstract

Rare earth elements (REE) have become essential in high- and green-technologies. Their increasing use lead to the release of anthropogenic REE into the environment including aquatic systems. The limited data available on the aquatic ecotoxicology of REE indicate their biological effects are highly dependent on their speciation, posing challenges for a reliable environmental risk assessment (ERA). The current study assessed the influence of speciation on the toxicity of neodymium (Nd), gadolinium (Gd) and ytterbium (Yb) in the *Daphnia magna* mobility inhibition test (ISO 6341:2012). REE toxicity was assessed individually and in ternary mixture, in the absence and presence of dissolved organic matter (DOM). Speciation was predicted by modeling and REE bioaccumulation by *D. magna* was measured to better understand the relationship between REE speciation and toxicity. DOM decreased significantly the toxicity of Nd, Gd and the mixture towards this freshwater crustacean. This was explained by a lower REE bioaccumulation in the presence of DOM due to REE-DOM complexation, which reduced REE bioavailability. DOM effects on Yb toxicity and bioaccumulation were limited because of Yb precipitation. We show that the way of expressing EC50 values (based
on nominal, measured or predicted REE concentrations in solution) drastically changed REE
toxicity assessment and that these changes were influenced by REE speciation. This study
demonstrates for the first time that REE speciation, and especially REE-DOM complexation,
significantly influences REE bioaccumulation and toxicity towards *D. magna*. Our results have
implications for the subsequent ERA of REE.

**Keywords**

Rare earth elements; mixture; toxicity; bioaccumulation; speciation; dissolved organic matter

1 **Introduction**

Rare earth elements (REE) are a group of 17 metals including the lanthanide series, scandium
(Sc) and yttrium (Y). They are naturally present in the environment, constituting a chemical
group sharing similar characteristics (Feng et al., 2013). The group is divided essentially into
three subgroups based on their ionic radii: LREE (Light Rare Earth Elements), MREE (Medium
Rare Earth Elements), and HREE (Heavy Rare Earth Elements) but the division is sometimes
limited to LREE and HREE (Zepf, 2013). They are little known to the public although they are
used daily by everyone via smartphones, computers, cars, household appliances and more.
Since around 30 years, REE have become essential in high- and green-technologies (e.g. wind
turbines, solar panels, electrical vehicles) but their supply capacity is below the increasing
demand. Thus, REE are now considered as critical raw materials (European Commission,
2011). Despite their use in the production of clean energy, they are of growing ecotoxicological
concern because of their release into the environment during mining extraction, uses in
industrial and agricultural activities and because of e-waste management, among others
(Gwenzi et al., 2018). The presence of anthropogenic REE in aquatic systems was first
demonstrated with the release of gadolinium (Gd) contained in contrast agents used in magnetic
resonance imaging (MRI), disturbing natural REE biogeochemical cycles (Bau and Dulska,
Rare earth element applications, especially as permanent magnets, and associated releases in the environment are expected to increase in the future (Haque et al., 2014). However, still little is known about the fate and ecotoxicology of REE, which prevents the establishment of a reliable environmental risk assessment (ERA) (Blinova et al., 2020). Studies on REE toxicity and bioaccumulation in aquatic systems are scarce and focused mainly on lanthanum (La) and cerium (Ce) (Blinova et al., 2020). There are limited data on other REE, notably on neodymium (Nd), terbium (Tb) and HREE such as thulium (Tm) and ytterbium (Yb), which should thus be studied with priority, particularly LREE that are more abundant and bioaccumulated than HREE (Blinova et al., 2020). Most studies evaluated the individual effects of REE but not the combined effects of REE mixtures (Gonzalez et al., 2014) although different REE occur together in the environment. Missing data on the toxicity of some REE and their mixtures prevent the establishment of a consensus on the uniformity of different REE (Gonzalez et al., 2014). Moreover, biological effects observed with REE are heterogeneous (Blinova et al., 2020; Gonzalez et al., 2014). This can be explained partly by differences in test solution composition, which strongly influence REE speciation (i.e. the different chemical and physical forms of REE) and in consequence induces different biological effects (Barry and Meehan, 2000; Borgmann et al., 2005; Gonzalez et al., 2014; Vukov et al., 2016). Dissolved organic matter (DOM) is an ubiquitous component of aquatic systems known to influence the speciation, bioavailability and the subsequent toxicity of metals (Wood et al., 2011). DOM is taken into account in the definition of environmental quality standards of some priority metals (i.e. lead and nickel) through the application of the biotic ligand model (BLM) (European Parliament, 2013) in order to allow for a more realistic ERA (Rüdel et al., 2015). Although DOM effects on REE speciation and fate in water are well known (Davranche et al., 2017; Johannesson et al., 2004; Marsac et al., 2011; Pourret et al., 2007a, 2007b; Sonke and Salters,
few studies have investigated DOM effects on REE toxicity.

In the present work, we aimed for a better understanding of the influence of speciation on REE toxicity. To assess whether different elements of the REE group share similar toxicity and characteristics, we tested Nd (LREE), Gd (MREE) and Yb (HREE) individually and in mixture. The selected elements are of concern because of their human use (Nd as permanent magnet and Gd in MRI), their occurrence in aquatic systems (anthropogenic Gd from MRI (Louis et al., 2020)) and missing ecotoxicological data (Yb and Nd are among the least studied REE (Blinova et al., 2020)). REE toxicity was assessed on the key freshwater zooplankton species, *Daphnia magna*, using the mobility inhibition test guideline (ISO, 2012). REE speciation was predicted by modeling and its influence on REE toxicity was investigated in the ISO solution modified or not by the addition of DOM. Because speciation regulates exposure, bioavailability and toxicity, the EC50 values were calculated and expressed in different ways, based on nominal, measured and predicted REE concentrations in solution. In addition, REE bioaccumulation by *D. magna* was analysed to better understand the relationship between speciation and toxicity.

2 Materials and Methods

2.1 Rare Earth Elements (REE) and Dissolved Organic Matter (DOM) preparation

REE stock solutions were prepared by dissolution in MilliQ water (5 g L\(^{-1}\) REE salt; neodymium nitrate (Nd(NO\(_3\))\(_3\).6H\(_2\)O), gadolinium chloride (GdCl\(_3\).6H\(_2\)O), ytterbium chloride (YbCl\(_3\).6H\(_2\)O); all purity > 99%; Sigma Aldrich). Salts of chlorides and nitrates were used because the complexation of Nd, Gd and Yb with Cl\(^-\) and NO\(_3^-\) is negligible. REE concentrations were measured in the stock solutions and no precipitation was observed. For each REE concentration tested, an intermediate solution was prepared by dilution of the REE stock solution so that an equivalent volume of REE solution could be added to all test flasks.
The used DOM had been obtained from Wageningen University, by purification of groundwater from Netherlands. It is mainly composed of fulvic acid (>80%) as determined by the method of van Zomeren and Comans, (2007). The stock solution was stored in the dark at 5°C. We worked with a dissolved organic carbon (DOC) concentration of 8 mg C L\(^{-1}\) because this is representative of concentrations found in freshwater systems such as rivers (2-25 mg C L\(^{-1}\)) and lakes (2-30 mg C L\(^{-1}\)) (Thurman, 1985). The DOM stock solution was diluted in MilliQ water to obtain the desired DOC concentration of 8 mg C L\(^{-1}\) in the test flasks.

### 2.2 Daphnia magna mobility inhibition test

The mobility inhibition of the freshwater crustacean *D. magna* was evaluated following the protocol described in detail in the European NF EN ISO 6341:2012 guideline (ISO, 2012). Complementary information about the protocol can be found in the international equivalent OECD 202:2004 guideline (OECD, 2004). Briefly, the toxicity of Nd, Gd and Yb was first tested individually (single test) and afterwards in ternary equitoxic mixture (mixture test), which means that each element was present at the same fraction of their own individual toxicity (Minguez et al., 2018). Therefore, the REE concentrations tested in the mixture were selected according to the nominal EC\(x\) values (EC\(_5\), EC\(_{10}\), EC\(_{30}\), EC\(_{50}\), EC\(_{65}\), EC\(_{75}\), EC\(_{80}\)) of each REE determined in the single tests. All tests included five REE concentrations inducing from 0 to 100% inhibition and a control (no REE).

In addition, all tests were performed in the absence (0 mg C L\(^{-1}\) DOC, denoted DOM-) and presence (8 mg C L\(^{-1}\) DOC, denoted DOM+) of DOM to modify REE speciation and to assess its influence on REE toxicity. In the single tests, REE concentrations were the same in DOM- and DOM+. Prior to the test, the flasks (glass test tubes, 15 mL capacity) were exposed to 10 mL of ISO solution (294 mg L\(^{-1}\) CaCl\(_2\), 2H\(_2\)O; 123 mg L\(^{-1}\) MgSO\(_4\), 7H\(_2\)O; 65 mg L\(^{-1}\) NaHCO\(_3\); 6 mg L\(^{-1}\) KCl) spiked with REE during at least 12 h in order to equilibrate glass wall adsorption sites with REE and to limit REE losses during the test. After this preconditioning,
the flasks were emptied and the solution was renewed. Then, ISO solution, DOM (in DOM+ tests) and REE were added consecutively to the flask constituting the test solution. The daphnids were immediately added after REE addition in order to enhance REE exposure before REE precipitation, which occurs relatively fast (Romero-Freire et al., 2019). We considered the beginning of the test (t0) after adding the daphnids to the test solution.

Neonates (less than 24h), originating from our laboratory culture, were exposed to REE during 48 h at 20°C (+/-2°C) in the dark. At the end of the test, after 48h exposure (t1), REE toxicity was assessed by evaluating D. magna mobility. The daphnids were considered as not mobile when they did not move during the 15 seconds following a gentle tube shaking. A test was performed with at least four replicates (1 replicate = 5 daphnids) and repeated twice.

Prior to the addition of DOM, REE and daphnids, the pH of the ISO solution was measured and adjusted, with a 3.2% HCl solution, at 6.5 instead of 7.8 (recommended in the ISO guideline) in order to enhance REE solubility and bioavailability. Such pH value (6.5) reflects naturally acidic freshwaters, which tend to have higher DOC concentration (Thurman, 1985). The pH was measured again at t1 in the solutions of the control and extreme concentrations as recommended in the OECD guideline (OECD, 2004). The pH in the solution of intermediate concentrations was estimated from the equation of the linear correlation between pH values and total REE concentrations measured at t1 (Table S1).

Several tests with the reference substance, potassium dichromate, indicated that the EC50_{24h} of the latter was included in the range, [0.6 – 2.1] mg L\(^{-1}\), recommended by the ISO guideline (ISO, 2012), which validated the reliability of the test conditions.

### 2.3 REE concentration measurement and analysis

For one of the two tests performed, REE concentrations in the test solution and in daphnids were measured after 48 h exposure by Inductively Coupled Plasma - Mass Spectrometry (ICP-
The test solution was filtered using a mix cellulose ester filter (MF-Millipore, reference: HAWP04700) in order to separate the particle phase (>0.45 µm) retained by the filter and the dissolved phase (<0.45 µm) constituting the filtrate. For each concentration tested, the test solution of all replicates was filtered on a unique filter and the filtrates were pooled. The REE concentration was measured in the pool of filtrates. We consider this concentration as the measured dissolved concentration at t1 (denoted [REEdiss]). In addition, the amount of REE retained on the filter was quantified after mineralization and the concentration of particulate REE in the test solution was recalculated and added to the dissolved concentration to determine the total REE concentration at t1 (denoted [REEtot]). Because measured in the pool of replicates, the unique value of [REEdiss] and [REEtot] obtained for each concentration represents an average value. Prior to ICP-MS analysis, the filtrate was acidified at 1% [v/v] with HNO₃ 69% in Milli-Q water and stored at 4°C; filter membranes were digested with 2 mL HNO₃ 65% (Fischer Scientific) at 80°C until complete mineralization.

REE recovery at t1 was calculated as the ratio between [REEtot] and the nominal concentration at t0. More than 90% of [REEtot] values did not remain within 80-120% of the nominal concentration (recovery <80% or >120%) (Table S1), thus the toxicity results were systematically based on measured concentration as recommended in the ISO guideline (ISO, 2012) and REE exposure concentrations were corrected calculating the geometric mean concentration according to Romero-Freire et al. (2019):

\[ [\text{REE}]_{\text{mean}} = \sqrt{(C_0 \times C_1)} \]  

(1)

with C0 being the nominal concentration at t0 (nominal was used instead of measured because REE concentration at t0 was not measured here) and C1 being the measured (total or dissolved) concentration at t1. When using [REEtot] to calculate the geometric mean, the latter is denoted [REEtot]_{mean} and when using [REEdiss] it refers to [REEdiss]_{mean}. For substances such as REE
where the exposure concentration decreases significantly during the test (e.g. Blinova et al., 2018; Romero-Freire et al., 2019; Vukov et al., 2016; Weltje et al., 2002), the mean concentration represents more properly the real exposure along the test than using the unique concentration at the beginning or the end of the test (OECD, 2000).

For each concentration tested, the daphnids of all replicates (≥ 20 daphnids) were pooled and the REE concentration was measured in this pool (denoted [REE]_{D.magna}) in order to estimate REE bioaccumulation. The organisms were dried at 50°C during 24 h and digested with 1 mL of HNO\textsubscript{3} 65% at 80°C before analysis. The Bioconcentration factor (BCF) was calculated to compare the bioaccumulation between the different exposure conditions using the formula:

\[
BCF = \frac{[\text{REE}]_{D.magna}}{[\text{REE} \text{diss}]_{\text{mean}}} \tag{2}
\]

For ICP-MS analysis, all samples, blanks and standards were diluted to a final concentration of HNO\textsubscript{3} at 2%. The following isotopes were measured: \(^{146}\text{Nd}, ^{157}\text{Gd}, ^{173}\text{Yb}.\) Rhenium (\(^{187}\text{Re}\)) was used as internal standard. Limits of detection (LOD) and quantification (LOQ) were determined and ranged from 0.1 to 0.3 µg L\textsuperscript{-1} for each element in aqueous samples and from 0.01 to 0.04 mg g\textsuperscript{-1} dry weight in solid samples (daphnids, filters). Analytical and procedural blanks were prepared and analysed using the same analytical procedure as for samples. The accuracy of the analytical protocol was validated using international certified materials (BCR-667 and BCR-668) consisting, respectively, of estuarine sediments and mussel tissues from LGC standards. The recovery of Nd, Gd and Yb were respectively 111, 113 and 100%.

2.4 Geochemical speciation modeling

PHREEQC (version 2) (Parkhurst and Appelo, 1999) is a computer code based on an ion-association aqueous model, which was designed to perform speciation and saturation-index calculations in water. The thermodynamic database “Minteq.v4.dat” provided with PHREEQC
was used. This database has been updated by the incorporation of the well-accepted reactions and stability constants at 0 M ionic strength and 25°C for REE inorganic anion complexation relevant to the present work (Table 1 and references therein). Ionic strength corrections have been performed with the Davies equation. REE binding modeling to DOM was considered using the humic-ion binding model “Model VII” (Tipping et al., 2011). PHREEQC-Model VII coupling is described thoroughly elsewhere (Marsac et al., 2017, 2014). Briefly, Model VII assumes that the complexation of ions by humic acids (HA) occurs through various discrete groups (carboxylic and phenolic groups), which can form either mono-, bi- or tri-dentate binding sites. Because HA are large and negatively charged polyelectrolytes or colloids, electrostatic effects are also accounted for the quantification of metal ions-HA binding (Tipping et al., 2011). Because no parameter is available for REE complexation to fulvic acids (FA), the most recently optimized binding parameters for REE and HA were used (Marsac et al., 2021) as a proxy of REE-FA binding parameters. By using [REEtot] and pH values measured at t1 and accounting for potential REE sorption to the flask, we performed simulations to determine each REE distribution between three distinct compartments: (i) a solid phase of potential REE(OH)\(_3\)(s) precipitates, (ii) a colloidal phase that includes REE bound to HA and (iii) truly dissolved REE that include REE aquo-ions (REE\(^{3+}\)) and all dissolved complexes (with OH\(^-\), CO\(_3^{2-}\), Cl\(^-\), etc.).

### 2.5 Data analysis

The dose response-curves, the ECx values and their confidence interval (95% certainty) were obtained using R (version 3.6.1), package “drc” (Ritz et al., 2015). A log-logistic model with two parameters (LL.2) was used to fit the data. Because speciation affects REE exposure and bioavailability, the EC50 were calculated and expressed based on the nominal (theoretical), the geometric mean of total ([REEtot]\(_{\text{mean}}\)) and dissolved ([REEdiss]\(_{\text{mean}}\)) concentrations, and the predicted free ion concentrations (calculated by modeling) to assess the influence on REE
toxicity assessment. The comparison of EC50 values was based on confidence interval overlap. The relationship between two variables was evaluated through a simple linear regression test with the function “lm” in R.

3 Results

3.1 REE exposure concentrations and speciation

In the absence (DOM-) and presence (DOM+) of DOM, all concentrations of Nd, Gd and Yb measured in the water at t1 were lower than the nominal ones. The recovery was slightly higher in DOM+ (62-89%) than in DOM- (34-79%) but most of the time it was below 80% (Table S1). Therefore, REE exposure concentrations were corrected calculating the geometric mean of the total ([REEtot]mean) and dissolved ([REEdiss]mean) concentrations (cf section 2.3).

Nd and Gd presented a similar geochemical speciation with the absence of precipitation and an occurrence only in dissolved form (Table 2). On the contrary, Yb was calculated to be present in often precipitated form (i.e. Yb(OH)$_3$) between 21 and 38% in DOM- and between 12 and 31% in DOM+ (Table S1). With increasing Yb total concentrations, the fraction of precipitated Yb first increased and then decreased (Figure S1). In the mixture tests, Yb occurred only in dissolved form (i.e. no precipitation occurred) as well as Nd and Gd (Table S2).

In the dissolved phase, Nd, Gd and Yb, individually and in mixture, were present in the same forms, mainly as REE$^{3+}$ (7-74%), REECO$_3^+$ (1-53%) and REESO$_4^+$ (1-25%) (Table 2). In DOM+, the proportion of free ion REE decreased relatively to DOM-, by 12%, 20%, 7%, 13% for Nd, Gd, Yb and the mixture, respectively (Table S1).

The presence of DOM modified the geochemical speciation of all REE through the formation of REE-organic (REE-DOM) complexes. The speciation model predicted between 6 and 38% of total Nd (Gd 6-73%, Yb 6-58%, mixture 11-43%) were complexed to DOM (Table 2), with declining values at higher REE concentration in solution (Figure S1). The proportions
of Nd, Gd and Yb bound to DOM between single (Table S1) and mixture tests (Table S2) were relatively close.

### 3.2 REE bioaccumulation and toxicity

REE concentrations measured in the daphnids ranged from 2 to 137 mg g\(^{-1}\) (in DOM-) and from 3 to 109 mg g\(^{-1}\) (in DOM+) (Table 2) and were significantly related to the REE concentrations measured in solution (linear regressions: p-values < 0.05, Figure 1; Table S3).

Bioaccumulated concentrations tended to follow the order Nd > Gd > Yb (Table 2). Bioaccumulation decreased in DOM+ compared with DOM- for Nd, Gd, the mixture and, in a lesser extent, for Yb (Table 2). The respective mean BCF values were 2.8, 2.6, 2.1 and 1.3-fold lower in DOM+ than in DOM- for Nd, Gd, the mixture and Yb. The lower REE bioaccumulation in DOM+ is also visible by the regression line for DOM+ (in orange) being below the regression line obtained for DOM- (in blue) (Figure 1).

Mobility inhibition was positively related to REE concentration measured in the daphnids (linear regression: \(R^2=0.84\) and 0.76 in DOM- and DOM+ respectively, p-values < 0.05, Table S4) and to REE concentration in solution, which is visible by the dose response-curves (Figure 1). The EC50 values and their confidence interval based on nominal, [REE\(\text{tot}\)\_mean], [REE\(\text{diss}\)\_mean] and free ion concentrations are reported in the Table S5. In DOM-, the EC50 values of Nd, Gd and Yb in single and mixture tests ranged between 8.3 and 8.8 mg L\(^{-1}\) (nominal concentration), 4.7 and 6.2 mg L\(^{-1}\) ([REE\(\text{tot}\)\_mean]), 2.5 and 4.9 mg L\(^{-1}\) ([REE\(\text{diss}\)\_mean]) and between 0.6 and 1.9 mg L\(^{-1}\) (free ion concentration) (Figure 2). The EC50 confidence interval of the three REE overlapped excluding those of Yb when considering [REE\(\text{diss}\)\_mean] and free ion concentration (Figure 2). The EC50 values were 2.8, 1.9 and 1.3 fold higher in DOM+ than in DOM- for Nd, Gd and the mixture respectively (based on dissolved concentrations) (Figure 2). Their EC50 values were close and ranged from 10.4 to 12.8 mg L\(^{-1}\) (nominal concentration), 8.5 to 10.1 mg L\(^{-1}\) ([REE\(\text{tot}\)\_mean]), 4.7 to 6.3 mg L\(^{-1}\) ([REE\(\text{diss}\)\_mean])
and 2.1 to 2.9 mg L\(^{-1}\) (free ion concentration) (Figure 2). The lower toxicity in DOM+ is also visible by the dose-response curves for DOM+ (in orange) being below the curves obtained for DOM- (in blue) (Figure 1). On the contrary, Yb EC50 values were similar in DOM- and DOM+ and their confidence intervals and dose-response curves overlapped (Figures 1, 2). In DOM+, the toxicity (i.e. EC50 values) of Yb was higher than Nd, Gd and the mixture if considering nominal and free ion concentrations (Figure 2). In DOM- and DOM+, the EC50 values of the mixture were close to the mean of the EC50 values of the three single REE (Figure 2).

4 Discussion

In this work, we investigated the influence of REE speciation on the toxicity to a key freshwater zooplankton species, \(D.\) magna. To tackle this issue, we added DOM to the test solution and expressed REE EC50 values in different ways. REE bioaccumulation was analysed to better understand the relationship between speciation and toxicity. Nd (LREE), Gd (MREE) and Yb (HREE) were tested individually and in mixture to assess the uniformity of their effects.

4.1 REE toxicity individually and in mixture

Nd, Gd and Yb, individually and in mixture, showed a similar toxicity with EC50 values ranging in a relatively narrow interval (Figure 2). If considering nominal, \([\text{REE}_{\text{tot}}]_{\text{mean}}\) and \([\text{REE}_{\text{diss}}]_{\text{mean}}\) concentrations, the discrepancy between Nd, Gd and Yb EC50 values (in single and mixture tests) never exceeded a factor of 2 (Table S5). Our results corroborate the similar toxicity of La, Ce, Pr, Nd and Gd observed with \(D.\) magna (Blinova et al., 2018). The homogenous toxicity of REE is probably linked to their comparable physicochemical properties. Based on our EC50 values (expressed as \([\text{REE}_{\text{tot}}]_{\text{mean}}\) and \([\text{REE}_{\text{diss}}]_{\text{mean}}\)), Nd, Gd and Yb could be included in the same category (category 2: EC50 > 1 to \(\leq 10\) mg L\(^{-1}\)) of the classification of hazardous substances to the aquatic environment (United Nations, 2021). Such a range of REE concentrations (1-10 mg L\(^{-1}\)) can be found in stream water located in REE
mining areas (Liang et al., 2014; Liu et al., 2019). However, REE concentrations usually found in natural freshwaters are ranged between 30 to 3000 ng L$^{-1}$ with median values around 150 and 370 ng L$^{-1}$ for rivers and lakes respectively (Noack et al., 2014). According to the toxic values determined in the current study, the environmental risk caused by REE is mostly located in REE mining areas and to a lesser extent in wastewater treatment plant influent or downstream for hospital areas (González et al., 2015). However, additional toxicity data on other species belonging to different trophic levels (e.g. algae, fish) are necessary to realize a proper ERA of REE.

The toxicity of the mixture was similar to the toxicity of the individual REE. This can be explained by the similar chemical and physical behavior of REE when present individually or in mixture. Indeed, the speciation and bioaccumulation of Nd, Gd between single (Table S1) and mixture tests (Table S2) were relatively close. These results suggest no interactions between REE in mixture. Empirically, the absence of interactions lead to additive toxic effects in mixture, which is mostly the case for substances having similar toxicity (Kortenkamp et al., 2009), such as REE.

4.2 DOM influence on REE speciation, bioaccumulation and toxicity

The presence of DOM in solution changed REE speciation, which significantly influenced REE bioaccumulation and toxicity, especially for Nd, Gd and the mixture. DOM modified REE speciation by the formation of REE-DOM complexes (Table 2). The decreasing proportions of REE-DOM complexes with increasing total REE concentrations (Figure S1) can be explained by both (i) the concomitant decrease in pH (Table S1) (ii) metal loading of DOM (saturation of the complexation sites) (Marsac et al., 2010). The complexation between REE and DOM reduced REE bioavailability and bioaccumulation because of a decreased proportion of free ion REE in DOM$^+$ solution (Table 2), which is largely accepted to reflect metal bioavailability (Di Toro et al., 2001). Our results corroborate those of MacMillan et al. (2019),
who suggested that DOM reduces REE bioavailability. They demonstrated in Canadian lakes that zooplankton accumulated less REE with decreasing REE/DOC ratio. Bioaccumulated metals are distributed at subcellular level between sensitive/toxic fractions (biologically active metals) and detoxified fractions (biologically inactive metals) (Wallace et al., 2003). Cardon et al. (2019) demonstrated that *D. magna* accumulated most yttrium (Y) (75%) in a detoxified form (as metal-rich granules), but Y concentrations measured (0.00002-0.055 mg g⁻¹ w.w.) were much lower than the REE concentrations we measured (2-137 mg g⁻¹ d.w.). This can be explained by the lower concentrations they tested (0.2-1.2 mg Y L⁻¹) compared to our concentrations (0.4-28.4 mg REE L⁻¹). Indeed, we demonstrated that the higher REE concentration was in solution, the higher REE concentration was in *D. magna* (Figure 1). Our results are in agreement with the positive correlation found between REE accumulation by zooplankton and REE concentration measured in natural waters (MacMillan et al., 2019). It is likely that we underestimated bioaccumulation because mortality occurred, especially at higher tested REE concentrations. Died daphnids will have a lower bioaccumulation period compared to alive daphnids. The consideration of alive daphnids only would have enhanced the relationship between REE bioaccumulation and REE concentration in solution.

REE bioaccumulation was related to REE toxicity (Table S4). Indeed, lower toxicity was observed with lower REE bioaccumulation. The presence of DOM divided by 2.1-2.8 the bioaccumulation and by 1.3-2.8 the toxicity of Nd, Gd and the mixture towards *D. magna*. Our results are in accordance with previous works studying DOM influence on the toxicity of Tm (Loveridge et al., 2021) and Dy (Vukov et al., 2016) towards the crustacean *Hyalella azteca*. 9.3 mg C L⁻¹ from Suwannee River divided by 2 Dy toxicity (Vukov et al. 2016). Compared to these works, our approach is specific in combining speciation, bioaccumulation and toxicity towards *D. magna*. To our knowledge, only Aharchaou et al., (2020) also conducted the simultaneous investigation of DOM effects on speciation, bioaccumulation and resulting
toxicity of REE towards a microalga species. They showed that malic acid, nitrilotriacetic acid (NTA) and iminodiacetic (IDA) decreased Ce and La uptake and toxicity towards *Chlorella fusca* because of REE complexation with the organic ligands. A reduction of REE (Sm, Nd, La, Ce, Sc, Y, Eu, Tm) bioavailability and uptake in the microalga *Chlamydomonas reinhardtii* has been demonstrated in the presence of different organic ligands such as FA (El-Akl et al., 2015; Rowell et al., 2018), HA (Rowell et al., 2018), malic and citric acid (Tan et al., 2017; Yang et al., 2014; Yang and Wilkinson, 2018; Zhao and Wilkinson, 2015), diglycolic acid (Tan et al., 2017) and NTA (Nitrilotriacetic acid) (Zhao and Wilkinson, 2015). The attenuating effects of DOM on metal bioavailability and toxicity in aqueous media are well documented (Wood et al., 2011). Examples are reported for silver on microalgae (Paquet, 2007), for copper on crustaceans (Kramer et al., 2004), for zinc on bivalves (Vercauteren and Blust, 1996), and for lead and cadmium on fish (Schwartz et al., 2004). Our work demonstrates for the first time that DOM could also mitigate Nd and Gd (individually and in mixture) bioaccumulation and toxicity towards *D. magna*.

Contrary to Nd and Gd, DOM did not influence Yb toxicity and bioaccumulation. The calculated concentration of Yb$^{3+}$ in DOM+ and DOM- are similar (Table S1). In fact, contrary to Nd and Gd, Yb partly occurred as Yb(OH)$_{3(s)}$ solid form (Table 2), which controls the concentration of Yb$^{3+}$ in solution. On the contrary, Nd$^{3+}$ and Gd$^{3+}$ concentrations are controlled by the complexation with the DOM. The lower bioaccumulation of Yb relative to Nd and Gd would be explained also by Yb(OH)$_{3(s)}$ precipitation in single tests.

The described effects of DOM on REE bioaccumulation and toxicity are likely even stronger in natural waters where REE concentrations are much lower (ng L$^{-1}$) than those we tested (mg L$^{-1}$). The relative amount of REE bound to DOM strongly increases with decreasing REE/C ratio (Marsac et al., 2010), showing that the REE concentration in solution influences the binding of REE to DOM. At environmental REE/C ratios, we can expect a higher
complexation of Yb to DOM because the few strong binding sites are preferentially complexing 
HREE (Marsac et al., 2010).

4.3 Implications of speciation on REE toxicity assessment

By adding DOM, we demonstrated that test solution composition significantly 
influenced REE toxicity because it determines REE speciation. Similarly, water hardness 
reduces REE toxicity (Barry and Meehan, 2000; Borgmann et al., 2005; Cardon et al., 2019).

Solution composition also influences REE uptake mechanisms, and thus REE toxicity. The 
toxicity of Dy towards H. azteca was reduced with increased Ca and Na concentrations and 
lower pH, explained by competition between Ca$^{2+}$, Na$^{2+}$, H$^{+}$ and Dy$^{3+}$ for the binding to the 
biotic ligand (Vukov et al., 2016). Test solution variability can partly explain the heterogeneity 
of REE EC50 values reported in acute toxicity studies on crustaceans, which range from 9.4 to 
122.4 mg L$^{-1}$ (nominal concentration), from 0.043 to 5 mg L$^{-1}$ (measured total concentration) 
and from 0.3 to 1.5 mg L$^{-1}$ (measured dissolved concentration) (Table S5). Therefore, solution 
composition and speciation should be considered in the assessment of REE toxicity. Based on 
the same test solution composition, our results corroborate those of Gonzalez et al. (2015) and 
Ma et al. (2016) (Table S5). By contrast, the EC50 values (based on measured concentrations) 
determined in other studies (Blinova et al., 2018; Galdiero et al., 2019) using the same solution 
are much lower (by more than 10 fold) than those we found in the current study (Table S5). 
This may be explained by a significant REE precipitation reported in the study of Blinova et al. 
(2018), which might have caused high variations in REE concentration measurements, making 
an exact identification of EC50 values based on measured concentrations difficult.

We demonstrate that solution composition and the subsequent speciation may significantly 
affect REE exposure concentrations and bioavailability. Subsequently, the EC50 values were 
calculated according to nominal, [REEtot]$_{\text{mean}}$, [REEdiss]$_{\text{mean}}$ and predicted free ion 
concentrations in order to evaluate the influence on toxicity assessment. Nd, Gd and Yb tested
individually or in mixture, with or without DOM exhibited EC50 values in the following order: nominal > \([\text{REE}_{\text{tot}}]_{\text{mean}}\) > \([\text{REE}_{\text{diss}}]_{\text{mean}}\) > predicted free ion (Figure 2). This expected pattern has been observed also in other studies (Table S5). In the current work, the predicted free ion EC50 are on average 8-fold lower than nominal EC50, and up to 16-fold lower for Yb in DOM+ (Figure 2). This gap between EC50 values is highly relevant because it can strongly influence the subsequent ERA. The way of expressing EC50 should thus be selected with caution.

Nominal concentration is not suitable because the concentrations of Nd, Gd and Yb measured in the water at the end of the test were drastically lower than nominal ones (Table 2). This can be explained by REE adsorption on glass material and/or by REE precipitation (Blinova et al., 2018; González et al., 2015; Romero-Freire et al., 2019). The preconditioning of the test flask may have reduced but not completely avoided REE adsorption on flasks. According to the classification of hazardous substances to the aquatic environment (United Nations, 2021), Nd and Gd in DOM+ would be classified in the category 3 (EC50 > 10 to ≤ 100 mg L\(^{-1}\)) if considering nominal concentrations and in the category 2 (EC50 > 1 to ≤ 10 mg L\(^{-1}\)) if considering \([\text{REE}_{\text{tot}}]_{\text{mean}}\) and \([\text{REE}_{\text{diss}}]_{\text{mean}}\) (Figure 2). Consequently, the use of nominal concentrations can lead to underestimation of REE toxicity (Gonzalez et al., 2014; Vukov et al., 2016).

Measured total concentration does not seem appropriate, neither, because REE tend to complex, precipitate and form insoluble species supposed to be not or little bioavailable and thus not toxic (Blinova et al., 2020; Gonzalez et al., 2014). Therefore, we consider that the use of measured dissolved concentration (referring in the current study to \([\text{REE}_{\text{diss}}]_{\text{mean}}\), which includes the measured dissolved concentration at t1) is probably the most suitable way to express REE EC50. This was also suggested by Vukov et al. (2016). The water framework directive 2013/39/EC (European Parliament, 2013) recommended the use of measured dissolved concentration (<0.45 µm) to express the environmental quality standards of the
priority metals Pb, Cd, nickel and mercury. This is more reliable and conservative because it represents real concentration (measured), with higher bioavailability (dissolved) even if not all metal dissolved species are bioavailable. Accumulation and toxicity of metals can usually be predicted by the free ion concentration (Allen et al., 1980). The latter can be determined either experimentally, or by modeling. The experimental determination of the free metal concentrations is obviously the most reliable approach (Janot et al., 2021; Khan et al., 2017; Rowell et al., 2018). Yet, it has several drawbacks: (i) the measurements are rather expensive and time consuming, and (ii) data obtained are highly conditional because they are only valid for the investigated system and do not apply to other environmental conditions. By contrast, geochemical speciation modeling is a solution, but the data are subjected to several sources of uncertainty or mistakes made by the user of speciation codes:

(i) A complete set of the relevant reactions and thermodynamic constants must be used to perform the calculations (see e.g. Table 1 for the present work). Available default databases with speciation codes do not necessarily include all of them for all metal ions. For example, a closer look to the database provided in Visual Minteq revealed that only one hydrolysis constant and one complex with carbonate for the REE are considered.

(ii) Besides experimental uncertainties associated to any aqueous reaction constants, the value of a solubility product, used to predict mineral formation/precipitation, is supposed to vary with the size of the (nano)particles (Auffan et al., 2009; Schindler, 1967), which is difficult to determine when formed in ecotoxicological tests.

(iii) The input data are of high importance. For example, the use of nominal or measured total REE concentrations might affect the saturation index with respect to REE-mineral phase or REE-DOM loading and, hence, REE calculated speciation. Another crucial input parameter is the pH. Our calculations were based on pH values at t1 but did not take into
account pH evolution between t0 and t1. This evolution might impact REE speciation because pH was in the crucial range (6.5-7.5) for REE precipitation.

(iv) The REE-DOM model used in the present study is the most recently updated model considering REE-DOM interactions. However, because of the use of generic DOM parameters, Model VII does not consider the variability in DOM reactivity with respect e.g. to its origin.

Despite these challenges the recently optimized humic-ion binding Model VII (Marsac et al., 2021) enabled the determination of relatively close EC50 values (based on free ion concentration) between DOM- and DOM+ (Figure 2). This result is consistent if considering the free ion as the only metal form able to react with the biotic ligands, being taken up, and inducing toxicity, as suggested by the BLM (Di Toro et al., 2001). With all uncertainties related to the speciation presented above, it is clear that modeling the toxicity of REE using BLM remains challenging. In fact, most studies that attempted to apply the BLM to REE in the presence of DOM faced obstacles. The BLM largely underestimated REE uptake (Rowell et al., 2018; Tan et al., 2017; Yang et al., 2014; Yang and Wilkinson, 2018; Zhao and Wilson, 2015) and/or predicted an EC50 significantly lower in the presence of DOM compared to in the absence (Aharchaou et al., 2020; Vukov et al., 2016; Yang and Wilkinson, 2018). However, speciation modeling results might have been subjected to the uncertainties listed above. Otherwise, BLM faces new challenges related to (i) the consideration of REE-DOM complex toxicity, as well as of the nanoparticles formed in the presence of DOM, and (ii) the consideration of mixtures (mixture of REE and mixture of single REE species).

5 Conclusion

To assess the uniformity of the REE group, Nd (LREE), Gd (MREE) and Yb (HREE) were tested individually and in mixture in D. magna mobility inhibition test (ISO, 2012). Yb showed some differences in terms of speciation and bioaccumulation relative to Nd and Gd. However,
the three REE, individually and in mixture, exhibited a homogeneous toxicity with EC50 values falling within a close range. Our results are in accordance with the review of Blinova et al. (2020) on REE aquatic toxicity, which concludes that REE could be considered as a uniform group in the context of ERA despite some slight differences between light and heavy REE. The differences of electron configuration and atomic radius size between LREE, MREE and HREE did not seem to influence much REE toxicity.

The influence of speciation on REE toxicity was evaluated by adding DOM in solution and by calculating EC50 values in different ways (using nominal, measured and predicted concentrations). The geochemical speciation model predicted that DOM complexed a relevant proportion (6-73%) of total REE. The complexation between DOM and REE reduced the bioavailability and divided by 2.1-2.8 fold the subsequent bioaccumulation of Nd, Gd and the mixture, which explained their reduced toxicity by 1.3-2.8 times in DOM+. However, Yb toxicity was unchanged in DOM+, because similar calculated Yb$^{3+}$ concentrations were determined in DOM+ and DOM-. Contrary to Nd and Gd, Yb was predicted to precipitate in the single tests (DOM+ and DOM-) in the form of Yb(OH)$_3$ (s), controlling Yb$^{3+}$ concentrations.

We demonstrated that REE speciation significantly influences the related toxicity. However, speciation is often not considered in studies on REE ecotoxicity probably because its measurement/estimation is challenging and because of few developed collaborations between ecotoxicologists and geochemists. In this work, the speciation of Nd, Gd and Yb, individually and in mixture, was predicted in the absence and presence of DOM using the most updated model available. Despite some remaining uncertainties about REE speciation mainly due to missing data and model limitations, its predictions allowed explaining observed REE bioaccumulation and toxicity. The current work provides new data allowing a better understanding of DOM influence on REE speciation, bioaccumulation and toxicity towards a model animal. Relevant environmental risk assessment of REE should include DOM and
speciation, as both significantly influence REE toxicity. This work highlights the relevance of a combined approach from ecotoxicology and geochemistry in order to improve the ERA of (emerging) contaminants such as REE.

Acknowledgments

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Figure 1: Dose-response curves and bioaccumulation of Nd, Gd and Yb, individually and in mixture. $[\text{REE}_{\text{diss}}]_{\text{mean}} = \sqrt{(C_0 \times C_1)}$ with $C_0$ being the nominal concentration in solution at the test beginning ($t_0$) and $C_1$ being the dissolved concentration measured at the end ($t_1$). $[\text{REE}]_{D.magna} = \text{REE concentration measured in } D.\text{ magna at } t_1$. DOM$- = 0 \text{ mg C L}^{-1}$; DOM$+ = 8 \text{ mg C L}^{-1}$. Each dot corresponds to the mean of mobility inhibition of at least 4 replicates and the associated standard deviation is represented by the vertical bar. Each cross corresponds to the REE concentration measured at $t_1$ in a pool of daphnids ($\geq 20$ daphnids). The dashed line represents the regression line between $[\text{REE}]_{D.magna}$
and $[\text{REEdiss}]_{\text{mean}}$. $R^2 = \text{determination coefficient of the linear regression}$. Additional information about the regression analyses can be found in Table S3.
Figure 2: EC50 values of Nd, Gd and Yb, individually and in mixture, in the absence (blue) and presence (orange) of dissolved organic matter (DOM). The EC50 values are shown for four different conditions: nominal concentrations, the geometric means of total ([REEtot]$_{\text{mean}}$) or dissolved ([REEdiss]$_{\text{mean}}$) concentrations and the predicted free ion concentrations. Vertical bars represent 95% confidence intervals. DOM$-$ = 0 mg C L$^{-1}$; DOM$+$ = 8 mg C L$^{-1}$.
Table 1: Reaction and constant database for Nd, Gd and Yb. Chemical species refer to dissolved aqueous forms or solid form (denoted (s)). *Average value between fresh and aged solids. References: 1 = (Klungness and Byrne, 2000); 2 = (Lee and Byrne, 1992); 3 = (Luo and Byrne, 2004); 4 = (Luo and Byrne, 2001); 5 = (Spahiu and Bruno, 1995); 6 = (Diakonov et al., 1998)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Nd</th>
<th>Gd</th>
<th>Yb</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{REE}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{REEOH}^{2+} + \text{H}^+ )</td>
<td>-8.18</td>
<td>-7.83</td>
<td>-7.24</td>
<td>1,2</td>
</tr>
<tr>
<td>( \text{REE}^{3+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{REE(OH)}_2^{+} + 2\text{H}^+ )</td>
<td>-17.04</td>
<td>-16.37</td>
<td>-15.74</td>
<td>1,2</td>
</tr>
<tr>
<td>( \text{REE}^{3+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{REE(OH)}_3^{+} + 3\text{H}^+ )</td>
<td>-26.40</td>
<td>-25.28</td>
<td>-23.85</td>
<td>1,2</td>
</tr>
<tr>
<td>( \text{REE}^{3+} + \text{HCO}_3^- \rightleftharpoons \text{REEHCO}_3^{2+} )</td>
<td>2.28</td>
<td>2.36</td>
<td>2.53</td>
<td>3</td>
</tr>
<tr>
<td>( \text{REE}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{REECO}_3^{+} )</td>
<td>7.28</td>
<td>7.39</td>
<td>7.81</td>
<td>3</td>
</tr>
<tr>
<td>( \text{REE}^{3+} + 2 \text{CO}_3^{2-} \rightleftharpoons \text{REE(CO}_3^2)^- )</td>
<td>12.17</td>
<td>12.48</td>
<td>13.3</td>
<td>3</td>
</tr>
<tr>
<td>( \text{REE}^{3+} + \text{Cl}^- \rightleftharpoons \text{REECl}^{2+} )</td>
<td>0.65</td>
<td>0.65</td>
<td>0.65</td>
<td>4</td>
</tr>
<tr>
<td>( \text{REE}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{REESO}_4^{+} )</td>
<td>3.5</td>
<td>3.4</td>
<td>3.3</td>
<td>5</td>
</tr>
<tr>
<td>( \text{REE}^{3+} + 2 \text{SO}_4^{2-} \rightleftharpoons \text{REE(SO}_4^2)^- )</td>
<td>5.1</td>
<td>5.1</td>
<td>5.1</td>
<td>5</td>
</tr>
<tr>
<td>( \text{REE(OH)}_3^{(s)} + 3\text{H}^+ \rightleftharpoons \text{REE}^{3+} + 3\text{H}_2\text{O} )</td>
<td>18.28</td>
<td>17.58*</td>
<td>16.14*</td>
<td>6</td>
</tr>
</tbody>
</table>
Table 2: REE concentrations measured and predicted in test solution and in *Daphnia magna*. All REE concentrations were measured at the end of the test (48h = t1). DOM- = 0 mg C L\(^{-1}\); DOM+ = 8 mg C L\(^{-1}\). REE recovery corresponds to the ratio between total concentration measured at t1 and nominal concentration at t0. REE distribution (%) among the truly dissolved, colloidal (denoted (DOM)) and solid (denoted (s)) phases were calculated by modeling. \([\text{REEtot}]_{\text{mean}}\) and \([\text{REEdiss}]_{\text{mean}}\) correspond to the geometric mean \(=\sqrt{(C0\cdot C1)}\) where C0 refers to the nominal concentration at t0 and C1 refers to the total or dissolved concentration measured at t1. \([\text{REE}]_{D.magna}\) corresponds to the REE concentration measured at t1 in a pool of daphnids (≥20 daphnids). BCF = Bioconcentration factor = \([\text{REE}]_{D.magna} / [\text{REEdiss}]_{\text{mean}}\). Data represent the interval (min-max) of five values.

<table>
<thead>
<tr>
<th>REE</th>
<th>DOM</th>
<th>Nominal [REE] (mg L(^{-1}))</th>
<th>REE recovery at t1 (%)</th>
<th>([\text{REEtot}]_{\text{mean}}) (mg L(^{-1}))</th>
<th>([\text{REEdiss}]_{\text{mean}}) (mg L(^{-1}))</th>
<th>Predicted free ion [REE] (mg L(^{-1}))</th>
<th>Predicted main REE truly dissolved species (% tot)</th>
<th>Predicted REE colloidal and solid((s)) species (% tot)</th>
<th>Measured [REE] (D.magna) (mg g(^{-1}) dry weight)</th>
<th>BCF (L kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>DOM-</td>
<td>5.2-33.9</td>
<td>47-68</td>
<td>3.5-27.9</td>
<td>1.5-24.6</td>
<td>0.7-16.3</td>
<td>Nd(^{3+}).32-71</td>
<td>Nd(^{3+}).20-67</td>
<td>Nd(DOM) 6-38</td>
<td>34-137</td>
</tr>
<tr>
<td></td>
<td>DOM+</td>
<td>5.2-33.9</td>
<td>67-76</td>
<td>4.3-29.6</td>
<td>2.9-22.7</td>
<td>0.7-17.3</td>
<td>Nd(^{4+}).20-67</td>
<td>Nd(^{4+}).13-24</td>
<td>Nd(DOM) 6-38</td>
<td>16-109</td>
</tr>
<tr>
<td>Gd</td>
<td>DOM-</td>
<td>2.5-40.6</td>
<td>40-65</td>
<td>1.6-32.8</td>
<td>1.2-30.9</td>
<td>0.3-19.6</td>
<td>Gd(^{3+}).27-74</td>
<td>Gd(^{3+}).2-29</td>
<td>Gd(DOM) 6-73</td>
<td>7-120</td>
</tr>
<tr>
<td></td>
<td>DOM+</td>
<td>2.5-40.6</td>
<td>62-72</td>
<td>2.1-34.4</td>
<td>1.9-31.3</td>
<td>0.1-20.3</td>
<td>Gd(^{3+}).7-69</td>
<td>Gd(^{3+}).2-20</td>
<td>Gd(DOM) 6-73</td>
<td>3-96</td>
</tr>
<tr>
<td>Yb</td>
<td>DOM-</td>
<td>3.6-40.1</td>
<td>34-79</td>
<td>2.1-35.6</td>
<td>1.8-33.7</td>
<td>0.3-22.0</td>
<td>Yb(^{3+}).11-70</td>
<td>Yb(^{3+}).5-67</td>
<td>Yb(OH)(^{3+}) 0-38</td>
<td>2-96</td>
</tr>
<tr>
<td></td>
<td>DOM+</td>
<td>3.6-40.1</td>
<td>63-80</td>
<td>3.0-35.9</td>
<td>2.9-31.5</td>
<td>0.3-21.0</td>
<td>Yb(^{3+}).5-66</td>
<td>Yb(^{3+}).5-29</td>
<td>Yb(DOM) 6-58</td>
<td>2-76</td>
</tr>
<tr>
<td>Mix</td>
<td>DOM-</td>
<td>2.4-15.1</td>
<td>44-58</td>
<td>1.7-9.8</td>
<td>1.2-5.7</td>
<td>0.8-4.6</td>
<td>REE(^{3+}).27-63</td>
<td>REE(^{3+}).9-53</td>
<td>REE(DOM) 11-43</td>
<td>5-60</td>
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<tr>
<td></td>
<td>DOM+</td>
<td>3.5-18.1</td>
<td>76-89</td>
<td>3.1-15.0</td>
<td>2.4-8.5</td>
<td>1.8-6.9</td>
<td>REE(^{3+}).18-50</td>
<td>REE(^{3+}).15-26</td>
<td>REE(DOM) 11-43</td>
<td>11 49</td>
</tr>
</tbody>
</table>
Highlights:

- DOM modified speciation of REE (Gd, Nd, Yb) by the formation of REE-DOM complexes
- DOM decreased REE bioaccumulation probably by reducing REE bioavailability
- DOM significantly reduced the toxicity of Nd, Gd and mixture towards *Daphnia magna*
- Yb toxicity was not influenced by DOM probably because of Yb precipitation
- Speciation influences REE bioaccumulation and the subsequent toxicity
CRediT roles: **Nicolas Lachaux:** Conceptualization; Data curation; Formal analysis; Investigation; Resources; Validation; Visualization; Writing - original draft. **Charlotte Catrouillet:** Data curation; Formal analysis; Resources; Writing - review & editing. **Rémi Marsac:** Data curation; Formal analysis; Resources; Writing - review & editing. **Laurence Poirier:** Data curation; Formal analysis; Resources; Writing - review & editing. **Sandrine Pain-Devin:** Conceptualization; Supervision; Validation; Writing - review & editing. **Elisabeth Maria Gross:** Conceptualization; Supervision; Validation; Writing - review & editing. **Laure Giamberini:** Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Validation; Writing - review & editing.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: